

# Mull and Solvent Media for Infrared Use

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IN WORK on antibiotics, alkaloids, and plant regulators, the samples usually have been solids, and the methods most frequently used to obtain their infrared spectra have involved a medium. This led to frequent concern over what bands may have been obscured by the intense absorptions of the medium. In an earlier presentation and abstract (1), media were discussed that would relieve this situation by permitting complete supplementations. Attention was called to the special advantages of a mull system whereby hexachlorobutadiene supplements paraffin oil, and a solution system whereby tetrachloroethylene supplements carbon disulfide. Information concerning the use of these systems is recorded here.

## HEXACHLOROBUTADIENE AS A MULL MEDIUM

As shown by the dotted lines of Figure 1, paraffin oil of medicinal grade, as used for most mulls, gives intense obscuring absorptions near 3.4, 6.85, and 7.26 microns. In addition, there are less serious interferences near 2.4, 3.8, and 13.8 microns that often can be ignored but occasionally are disturbing. As shown by the solid line, the transmittance of hexachlorobutadiene exceeds that necessary for supplementation in each of these regions. The thickness in each case is 0.10 mm., which exaggerates the media effects by being roughly three times the thickness of the average mull preparation. It is evident that paraffin and hexachlorobutadiene supplements together can give complete supplementation at mull thicknesses without any interferences of a significant magnitude.

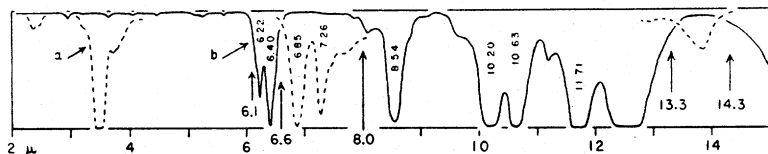


Figure 1. Supplementing Transmittances of Paraffin Oil and Hexachlorobutadiene

- A. Paraffin oil (heavy liquid petrolatum, U.S.P.), 0.10 mm.  
B. Liquid hexachlorobutadiene, 0.10 mm.

Perfluorokerosine (4, 11) has also been used to obtain spectra that are obscured by paraffin oils, and tests have shown that its useful region extends from below 2 to an absorption edge at about 7.20 microns when the thickness is 0.03 mm. Although the supplementing capacity is adequate for many special purposes, the utility of perfluorokerosine seemed inefficient or doubtful in the 7.3- and 13.8-micron regions, and therefore it was considered to be less complete than that of hexachlorobutadiene. The reduction of light scattering by perfluorokerosine was also believed to be less efficient because compatibilities resulting in partial solution or gelation of the sample seem less likely to occur, and the very low refractive index ( $n_D^{25}$  found, 1.3311) probably causes more abrupt changes of refraction at particle interfaces. The cost and availability of perfluorokerosine are also somewhat restrictive. It was concluded, therefore, that hexachlorobutadiene can advantageously replace perfluorokerosine for most mull purposes.

As widespread usage of hexachlorobutadiene has already resulted from the earlier announcement (1), it can now be recommended without reservation as a product whose general suitability has been proved by service. It is an oily liquid having a boiling point of 215° at 760 mm., and a refractive index ( $n_D^{25}$ ) of 1.5542 (4). Although the stability may not be as great as that of perfluorokerosine, it far exceeds the requirements. Fruhwirth (6)

reported that it behaves like a fully saturated compound; he could not polymerize it at 100 atmospheres' pressure, nor would it react with chlorine in the sunlight, with diene reagents like maleic anhydride, or with acids and bases. Other evidence of its unusual stability was reported by McBee and Hatton (10). The reagent used here was a commercially available product, of  $n_D^{25}$  1.5524, with the boiling point listed as 210–212°. This product did not need further purification and has shown no evidence of change in 3 years.

Because solubility and other properties specific to the sample are not limiting factors by the mull technique, the single supplementing combination of hexachlorobutadiene and paraffin oil adequately covers the entire general need for media in the mull field. Without further concern over media selections, these may be used to obtain qualitatively useful spectra of nearly every type of dry powderable sample. Highly bonded substances may give spectra that are not as sharp as desired, but this is not due to any fault of the media. Since the intensity of the CH bands as revealed by hexachlorobutadiene often is of understandable significance as a quantitative standard, having these and one additional band that is common to both supplements gives a basis for evaluating all intensities relative to each other, despite losses due to scattering. Although the accuracy is low, such evaluations are useful for estimating if a band is intense enough to indicate a specific group of the principal ingredient, as distinguished from minor bands that may arise from contamination or from secondary effects of fundamental vibrations.

When there is an unusual need to conserve the sample, the hexachlorobutadiene supplement can be done after the paraffin oil supplement on the same sample after the paraffin oil has been carefully flooded off with a volatile rinsing liquid like hexane.

Bonding patterns may be on a simpler basis in hexachlorobutadiene than in a paraffin oil medium, although such differences are of rare occurrence and have not been observed outside the 3-micron region. The most logical explanation seems to be that the hydrogen-containing oil has mild bonding properties, and the imbibing of this oil by the sample may force a change in weakly established bonding equilibria to give additional complexities. Although not observed, it seems reasonable to expect that imbibing an oil could influence the spectra of hydrates by displacing water in some instances.

## TETRACHLOROETHYLENE AS AN INFRARED SOLVENT

As reported earlier (1), and evident from published spectra (3, 8, 11), tetrachloroethylene can fill a critical need as an infrared solvent in the region from below 2 to 7.3 microns. It is possible to supplement completely the favorable region of carbon disulfide from 7.3 to beyond 15 microns. It seems evident, however, that the use of tetrachloroethylene has been hindered by troubles with impurities, and that there is a need to understand and take special precautions against these.

On exposure to light, air, and moisture, the unpreserved material becomes oxidized, resulting in contamination with trichloroacetyl chloride, phosgene, trichloroacetic acid (5, 7), and presumably hydrochloric acid. Ordinarily, the access of air in storage is not sufficiently prevented by glass stoppers. After contamination, a simple distillation does not adequately remove trichloroacetyl chloride, as the boiling range is similar. Trichloroacetyl chloride may be detected both by its odor and by a prominent band at 5.56 microns having a subsidiary peak at 5.72.

Commercially available tetrachloroethylene usually already contains a preservative, often about 0.5 to 1% alcohol (12), although advantages have been reported for pyrroles (9), and for thymol and other compounds (2). The purity has been satisfactory for infrared purposes when small portions were distilled as needed from a stock preserved with alcohol in brown bottles, and the first portion distilled was discarded. It seems advisable also to discard the excess remaining after use instead of attempting to preserve it. The need for such attention evidently will greatly restrict the use of tetrachloroethylene until more convenient means of maintaining its purity have been established, but for many purposes the advantages of complete supplementation warrant the extra effort.

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